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Physical and mechanical properties of a new edible film made of pea starch and guar gum as affected by glycols, sugars and polyols

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Highlights

- Pea starch/guar gum film incorporated with glycols, sugars, and polyols were developed
- The functional properties of the films were changed according to the type of plasticizer
- FTIR was used to study the interactions between the film components
- Monosaccharides showed a great potential to be used as plasticizer

ABSTRACT

The influence of different plasticizers (glycols, sugars and polyols) on the moisture sorption, mechanical, physical, optical, and microstructure characteristics of pea starch-guar gum (PSGG) film was studied. All plasticizers formed homogeneous, transparent, and smooth films, while PEG-400 did not produce film with suitable characteristics. Fourier transform infrared (FTIR) spectroscopy results indicated some interaction between plasticizers and the polymers. Scanning electron microscopy (SEM) observations of the films presented surfaces without cracks, breaks, or openings which were indicator of the miscibility and compatibility of employed plasticizers with PSGG films. The results showed that the films containing plasticizers with higher functional groups had lower equilibrium moisture content at $a_w < 0.4$. In general, a reduction in tensile strength and Young's modulus and an increase in elongation at break were detected when molecular weight of plasticizers and relative humidity increased in all film formulations. Films plasticized with monosaccharide showed similar mechanical properties to those with sorbitol, but lower solubility and water vapour permeability (WVP), higher transparency and moisture content than the sorbitol-plasticized films. The most noticeable plasticization effect was exerted by following order: glycerol > EG > PG > xylitol > fructose > sorbitol > mannitol > galactose > glucose > sucrose > maltitol.

Keywords: Pea starch; Guar gum; Edible films; Plasticizer; Monosaccharide; Polyol

1. Introduction

Petroleum-derived plastics in food packaging have been extensively developed, since they provide great protection for the product, are affordable, ease of manufacture and are lightweight and chemically resistant. However, due to stable carbon–hydrogen bond and very large polymer molecules in structure of petroleum-derived plastics, they are not biodegradable and remain in nature over a longer period of time [1]. The non-biodegradability and non-renewability nature of these plastics waste that generally produced from food packaging has resulted in environmental concern. Recently, extensive efforts have been made to develop biodegradable and eco-friendly packaging materials from renewable and inexpensive natural resources, due to the increased global concerns over preserving the natural environment and disposing the massive volume of petroleum-derived plastics in landfills. The development of biodegradable/edible films using numerous biopolymers in packaging will increase sustainability and decrease the adverse influence of plastic packaging on the environment owing to their biodegradability [2].

Various types of biopolymers have been explored as possible raw resources to develop biodegradable films and coatings. Application of edible films is one of the most affordable ways to control gas and moisture transmission, deterioration and loss of appearance, flavor, color, and nutritional values of food products and to preserve product stability, quality, safety, variety, and convenience for consumers during handling, storage and transportation [3].

The quality and application of edible films and coating for food products are influenced by their mechanical, barrier and sensorial characteristics, and their biochemical, physicochemical and microbiological stability, which in turn depend on film construction, its

preparation technology and the type of product to be preserved and on the circumstances under which the packaged product will be stored [4].

Starch as one of the most favorable agricultural raw resources, has been commonly recognized for edible films and coatings. Starch is the most plentiful storage glucan consists of anhydroglucose units: a linear chain molecule units linked with α -(1 \rightarrow 4) bonds named amylose and a branched molecule with α -(1 \rightarrow 6)-linked branch points and linear regions of α -(1 \rightarrow 4)-linked glucose units named amylopectin [5, 6]. The proportion of amylose:amylopectine content is main factor in starch edible films [7]. The linear structure of amylose in starch generally produces bioplastics with stronger and more flexible mechanical characteristics; whereas, the prevailing existence of branched structure of amylopectin results in the production of lower resistance bioplastics to tension and elongation [4].

The rising focus on resources for both currently accepted and innovative emerging applications leads to provoke attention in developing the function of available polymers for food packaging and in improving new polymeric systems [8]. In this regard, recent researches have explored new biocomposite edible films by incorporation of different hydrocolloids [9, 10].

In our previous studies, we found out that combination of guar gum and pea starch produce new biocomposite edible films with improved physical, optical, barrier and mechanical properties [11, 12], however, without adding plasticizer, they were brittle like other edible films from hydrocolloids. Our studies revealed that incorporation of 25% w/w glycerol based on the dry film matter in 100 mL of distilled water; make a composite film having adequate packaging characteristics. Glycerol as plasticizer molecule bring about reducing intermolecular forces along the polymer chains, consequently improving workability, or distensibility matrix biopolymer, as well as, increasing the chain extensibility and resistance

to fracture and dielectric constant [13]. Polyols, mono-, di- and oligosaccharides are the most mainly used plasticizers, which provide greater plasticizing impact to edible films of hydrocolloids [14]. The effectiveness of each plasticizer is associated with the molecular size, shape, number of free hydroxyl groups, spacing of oxygen atoms, water binding capability and the configuration of the biopolymer i.e. compatibility of the plasticizer with the film-forming polymer for homogeneous distribution in 3-dimensional structure of film [15-18].

In this context, a variety of plasticizers should be studied to elaborate their efficiency in preparing packaging films. To the best of our knowledge, there is no specific study on the effect of various plasticizers on film properties based on pea starch and guar gum. Therefore, this study aimed to comprehensively study film forming behavior of pea starch and guar gum in the presence of plasticizers containing different hydroxyl groups and to investigate the effect of the use these plasticizers on microstructure, moisture sorption, physical and mechanical characteristics of plasticized PSGG films.

2. Materials and methods

2.1. Materials

In all experiments, Canadian non-GMO yellow pea starch with 13.2% moisture, 0.2% protein, 0.5% fat and 0.3% ash was used (supplied by Yantai Shuangta Food Co., Jinling Town, China). Guar gum (E-412) was purchased from The Melbourne Food Ingredient Depot, Brunswick East, Melbourne, Australia. All other chemicals were obtained from Merck Millipore Pty. Ltd., Victoria, Australia.

2.2. Preparation of film-forming solution

PSGG films were prepared by casting with various plasticizers according to optimized amount of glycerol obtained from previous studies [11, 12]. Table 1 displays the plasticizers

selected for this study along with their characteristics; the difference in molecular size and shape determined by the different chemical conformation of each polymer imparts possibility to discover a variation of impacts on the films properties [19].

The film-forming solution was prepared by dissolving optimized amounts of pea starch (2.5 g), guar gum (0.3 g) and 25% w/w plasticizer (Table 1) based on the dry film matter in 100 ml degassed deionized water with gentle heating (about 40 °C) and magnetic stirring. The aqueous suspension was gelatinized at 90 °C for 20 min on a hot plate with continuous stirring. After gelatinization, the film solution was cooled to room temperature with mild magnetic stirring for 1 h to decrease air bubbles [20].

2.3. Swelling power (SP) and solubility index (SI)

The resulting dispersions were separately heated in a water bath at temperatures of 60, 70, 80 and 90 °C for 30 min. Suspension solution was cooled in ice before centrifugation at 15000 rpm for 30 min and the precipitate was calculated as W_0 . Both phases were dried at 105 °C for 16 h and the dry solids in precipitated paste (W_1) and supernatant (W_2) were weighed. Swelling power is the ratio of the weight of swollen starch granules after centrifugation (g) to their dry mass (g). Three replicates were used to measure swelling power and solubility index.

$$\text{Swelling power of starch} = \frac{W_0}{W_1} \quad (1)$$

$$\text{Solubility index of starch} = \frac{W_2}{W_3} \quad (2)$$

W_3 is the initial weight of starch [21].

2.4. Viscosity of film forming solutions

A viscometer (Brookfield, DV-IIIS04, Brookfield Viscometers, Ltd., Harlow, U.K.) was used to measure viscosity of films according to Saberi et al. [20].

2.5. Films preparation

Filmogenic suspensions (20 g) were cast onto Petri dishes (10 cm in diameter) and dried at 40 °C in an oven until reaching constant weight (about 24 h). Films were peeled-off carefully from Petri dishes and conditioned at 25 °C, 65% relative humidity (RH) for 72 h prior to further testing.

2.6. Film thickness and density

A digital micrometer (Mitutoyo Corp., Code No. 543-551-1, Model ID-F125, Japan; sensitivity= 0.001 mm) was used to calculate the thickness of the films. Measurements were randomly taken at 10 different positions for each specimen and the average value was calculated in mm and applied in the measurements of the mechanical properties and water vapor permeability (WVP). Film density was determined by dividing the weight of film by the film volume, where the film volume was evaluated by multiplying the film area by the thickness [20].

2.7. Moisture content and sorption isotherms

The moisture content (MC) of films was estimated gravimetrically using a ventilated oven at 105 °C until constant weight was reached.

Moisture adsorption isotherm of films was measured by exposing the 40 mm × 15 mm pre-weighed and dried specimens of films into desiccators containing the saturated solution of various salts creating varying relative humidity ranged from 0.11 to 0.93 at 25±2 °C (LiCl 0.113, CH₃COOK 0.225, K₂CO₃ 0.432, Mg (NO₃)₂ 0.529, NaNO₂ 0.654, NaCl 0.753, KCl

0.843, KNO₃ 0.936). Film samples were weighed at regular intervals until equilibrium was achieved. The mathematical models, Guggenheim–Anderson–de Boer (GAB) (Eq. (3)), Ferro-Fontan (Eq. (4)), and Peleg (Eq. (5)), was applied to fit sorption isotherm data and the values for monolayer were estimated from GAB equation [22]. Isotherm models can be explained by the equations given below:

$$M = \frac{M_0 \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w)(1 - K \cdot a_w + C \cdot K \cdot a_w)} \quad (3)$$

$$M = \left[\frac{\gamma}{\ln\left(\frac{\alpha}{a_w}\right)} \right]^{\frac{1}{r}} \quad (4)$$

$$M = K_1 a_w^{n_1} + K_2 a_w^{n_2} \quad (5)$$

Where M is the equilibrium moisture content at a specific water activity (a_w), M_0 is the monolayer value (g H₂O/g solids) while C, k, K_1 , K_2 , n_1 , n_2 , γ , r, and α are model constants.

The validation of the equations was assessed and compared using the correlation coefficient (R^2) and the mean relative percentage deviation modulus (M_e):

$$M_e = \frac{100}{n} \sum_{i=1}^n \frac{|M_{i,exp} - M_{i,pre}|}{M_{i,exp}} \quad (6)$$

Where $M_{i,exp}$ is the experimental value, $M_{i,pre}$ is the predicted value, n is the population of experimental data [22].

2.8. Water solubility

In this respect, 40 mm × 15 mm pieces of samples were dried in desiccator containing silica gel and weighed. Then, the same dried pieces of films were immersed in 50 ml of distilled water in screw capped containers, kept at room temperature under gentle agitation for 24 h, and filtered under vacuum through MN-640 m filter papers (Macherey-Nagel, Germany). The

residues were dried at 110 °C to constant weight and weighed to calculate the percentage of the solubility of the films by the following equation [14]:

$$\text{Solubility (\%)} = \frac{\text{initial dry weight} - \text{final dry weight}}{\text{initial dry weight}} \times 100 \quad (7)$$

Three replicates were carried out and averaged for each sample.

2.9. Water vapor permeability

Water vapor permeability (WVP) of films was examined gravimetrically using modified ASTM method E96-95 [23]. The film samples were sealed over the circular opening of cups which were half-filled with CaCl_2 (0% RH) and then located in a desiccator containing saturated NaCl solution (75% RH). WVP was measured from the weight gain of the test cup after every 2 h over a period of 24 h. A graph was plotted from the weight gain and time data according to linear regression ($r^2 > 0.99$) and the slope of straight line (g/m) was estimated. Water vapors transmission rate (WVTR) was calculated by dividing the slope with film surface area while WVP (g/Pa.m.s) was determined using the following formula [24]:

$$\text{WVP} = \text{WVTR} \frac{\text{Film thickness}}{\Delta P} \quad (8)$$

where ΔP is the water vapor pressure difference between the two sides of the film (Pa). WVP was measured for three replicated samples for each type of films.

2.10. Optical properties

Films transparency was examined using a UV-Vis Spectrophotometer (Varian Australia Pty. Ltd., Melbourne, VIC Australia) as shown by Saberi et al. [11].

A Minolta colorimeter (CR-300 series, Radiometric instruments Operations, Osaka, Japan) was used to determine the color of each film. The lightness (L^*) and chromaticity factors ' a^* '

(red-green) and ‘*b*’ (yellow-blue) were reported. The total color difference (ΔE) of samples were calculated [11]:

$$\Delta E = \sqrt{(L^* - L)^2 + (a^* - a)^2 + (b^* - b)^2} \quad (9)$$

where L^* , a^* , and b^* are the standard color parameter values and ‘ L ’, ‘ a ’, and ‘ b ’ are the color parameter values of the sample. The measurements were repeated six times for each film.

2.11. Mechanical tensile test

The mechanical properties of the films ($15 \times 40 \text{ mm}^2$) under various relative humidities (11, 43, 65 and 84 %) were evaluated using a Texture Analyzer (LLOYD Instrument LTD, Fareham, UK) with crosshead speed of 1 mm/s and initial grip distance 40 mm. Eight film specimens of each formulation were used for mechanical tests. The parameters obtained from force–deformation curves were percent elongation at break (deformation divided by initial probe length multiplying by 100, %), Young’s modulus (slope of force–deformation curve (N/mm) multiplying by initial sample length divided by film cross-section, MPa) and tensile strength (maximum force divided by film cross-section, MPa) [20].

2.12. Mechanical puncture test

The mechanical resistibility of films under sharp stress was determined by using a Texture Analyzer (LLOYD Instrument LTD, Fareham, UK). A 4 cm-diameter disk of films were cut and fixed in an annular ring clamp (3 cm diameter). A spherical probe of 1.0 mm diameter was moved vertically to the film surface at a constant speed of 1 mm/s until the probe passed through the film. Force (N) and deformation (mm) values at the puncture point were then recorded to express the puncture strength (N) and deformation (mm) of the films. For each sample, eight replicates were carried out [25].

2.13. Scanning electron microscopy (SEM)

Scanning electron micrographs with magnification of ~~(1000×)~~^(10000×) were taken by a scanning electron microscope (ZEISS, NSW, AU) at an accelerating voltage of 5 kV. Starch films were mounted on a bronze stub using double-sided adhesive tape, and the films were sputter coated with a layer of gold allowing surface visualization.

2.14. Fourier-transform infrared (FTIR) spectroscopy

The IR spectra of the films were implemented using an infrared spectrometer (FTIR) (Thermo Fisher Scientific Inc., Nicolet iS10, USA). The spectrums were obtained in at the range of between 450 and 4000 cm^{-1} , using 40 scans at a resolution of 4 cm^{-1} [26].

2.15. Statistical analysis

Analysis of variance was carried out and the results were separated using the Multiple Ranges Duncan's test ($P < 0.05$) using statistical software of Statistical Package for Social Science 16 (SPSS, Inc., NJ). All tests were performed at least in triplicate.

3. Results and discussion

3.1. Swelling power (SP) and solubility index (SI)

Differences in the SP and SI are shown in the Table 2. These values increased gradually by increasing temperature from 60 °C to 90 °C. The crystalline conformation of starch was destroyed in the presence of heat and excess water because of dissolving and melting of the double helices exist within the amorphous (double helices created between amylose chains and between amylose and the branched chains of amylopectin) and crystalline domains (double helices created between the outer branches of amylopectin), causing an increase in flexibility of amorphous region [27]. Additionally, the formation of hydrogen bonds between

water molecules and the exposed hydroxyl groups of amylose and amylopectin lead to an increase in swelling and solubility of granules. The solubility and swelling power of starch is a sign of the degree of starch chains interactions in the crystalline and amorphous areas. The ratio and properties of amylose and amylopectin such as degree of branching, length of branches, molecular weight distribution and structure of the molecules impact on the magnitude of this interaction [28]. For PSGG, SP and SI in the whole temperature range reduced compared with pea starch. This result demonstrated that guar gum restrained starch swelling and prohibited amylose leach out from native pea starch, representing the high interaction of guar gum with pea starch and the minimum phase separation, consequently improving the physical and mechanical properties of the film [10, 26]. At all temperatures, the SP and SI decreased in the presence of plasticizers, except PEG-400. The sugars gave lower SP and SI values than glycols. Their effect was determined by the size and flexibility of plasticizer molecules. Sugars reduced SP and SI by forming crosslinks (sugar bridges) between starch chains in the amorphous regions of a starch granule and stabilizing these regions. The larger sugar molecules, the longer gaps and the more crosslinks between chains produce [29]. Sucrose produced greater reduction in the SP and SI values than did monosaccharides. That could be anticipated, as sucrose has more hydroxyl groups than monosaccharides at the same molar concentration [30]. Among the sugar alcohols, maltitol resulted in the lowest value. This proposes that the hydroxyl group numbers in a sugar alcohol is a main reason in the changes in the SP and SI of starch. The differences in these values as affected by glycols suggest a possibility of an additional factor owing to molecular weight differences.

3.2. Viscosity of filmogenic suspensions

Pea starch should be gelatinized to produce biodegradable edible films, which is happened by heating pea starch granules in the presence of excess water till 90 °C for 20 min. With continued heating, an irreversible swelling occurs causing the interruption of intermolecular hydrogen bonds and disturbance of molecular order within the granules [1]. As a result, amylose and amylopectin molecules leach in to the water resulting in a significant increase in viscosity through hydrogen bonds [31]. When the film suspensions were subsequently cooled down to room temperature the viscosity of the pastes increased which was attributed to the re-association of amylose molecules (sometimes called short-term retrogradation) [32]. The film solution without plasticizer showed the higher viscosity because of dominant starch–starch and starch-gum associations (Table 3) [11]. By incorporation of plasticizers, the formation of double helices of amylose with amylopectin branches was destructed and the rigidity of the network was relatively reduced, causing lower apparent viscosity [33]. The viscosity of filmogenic suspensions was remarkably affected by the presence of plasticizers and the effect was found to depend on the molecular mass and the number of hydroxyl groups of plasticizer. The higher number of OH groups in the plasticizers, the higher viscosity values resulted, because of more chances for interaction with starch and guar gum chains as well as water and immobilization of a greater amount of water molecules [34]. By increasing the molecular weight of plasticizers, their ability to insert between adjacent polymeric chains decreased, so the interactions between the amylose and amylopectin molecules increased and the molecular mobility decreased, which resulted in the higher viscosity values. The film solution containing PEG-400 showed a reverse effect, because it holds less hydroxyl groups within its structure, which cannot efficiently situated between the polymeric chains [24]. This behaviour may be connected to the possible incompatibility between the PSGG and PEG-400.

3.3. Effect of plasticizer type

The primary study revealed that PSGG films prepared without plasticizer were very brittle and broke simply during peeling; therefore, did not characterize in the present study. Various types of plasticizer at 25% w/w of film dry basis were used to select the suitable plasticizer and to make sure that this amount of optimized plasticizer according to previous studies is proper for PSGG film formation. Plasticized PSGG films were peelable, flexible, smooth, homogeneous and transparent, except for those films comprising PEG-400. The number of air-bubbles appeared in unplasticized film were considerably decreased in the plasticized films representing the positive influence of plasticizers on the macromolecular attributes of PSGG films and the compatibility of these plasticizers with PSGG films. It was obvious that glucose, fructose, galactose and sucrose could plasticize as efficiently as the usually used polyols did. All the films containing glycols, sugars and polyols were uniform and clear without any crack. On the contrary, the films containing PEG-400 presented a white, opaque and rough surface. The films became brittle and were easily broken into pieces during drying. Due to the brittle structure, PEG-400-plasticized films were not used for further studies. This white opaque appearance might be because of the high molecular weight and relatively low content of hydroxyl groups within PEG-400, which cause physical exclusion, i.e., phase separation and incompatibility of PEG-400 with PSGG films referring to as “blooming” and “blushing” [24, 35]. Similar observations have been demonstrated for hydrocolloid films plasticised with PEG [14, 24, 35-37]. While, other plasticizer molecules incorporated successfully with pea starch chains and guar gum reduced the intermolecular attractions between molecules and produced extensible structure.

3.4. Film thickness and density

According to Table 3, the thickness of PSGG film samples significantly ($p < 0.05$) increased over the range of 0.094-0.206 as a response to the type of plasticizer. The increased thickness

of PSGG films by incorporation of plasticizers can be described by their function in disturbing the intermolecular bonds between polymer chains, which leads to rearrangement of the polymer configuration to a more expanded structure and thicker polymer film [14]. The thinnest film was film containing EG, while maltitol-plasticized film was the thickest film because of differences in their molecular weight. Among the monosaccharides, glucose produced thinner films due to the similarity of its chemical structure to the repeating units of starch. This structural homogeneity could bring about shortest spatial distance between starch molecules and closest packed matrix of polymers [38]. The molecular weight, composition and interaction between incorporated components and polymers in film structure determine differences in density [39]. The increase in density could be associated with the increased molecular weight of plasticizers.

3.5. Moisture content and sorption isotherms

The results of moisture content of film samples are illustrated in Table 3. The glycerol-plasticized film had the highest moisture content because of its highly hygroscopic nature [40]. Glycerol not only establishes direct interactions with starch, but also it has good water holding capacity to use the plasticizing activity of water molecules [38]. In comparison, the maltitol-plasticised blend films showed the lowest moisture content. This effect can be explained by the different molecular weight and molecular structure of plasticizers. Talja et al. [41] demonstrated that starch films containing a single lower molecular weight plasticizer have higher water content than films with a higher molecular weight plasticizer. The smaller plasticizer molecule, the better and easier it can insert between polymers chains to disturb the formation of polymer–polymer hydrogen bonds and increase free volume in polymer to adsorb more water [40]. However, it is interesting to note that EG-plasticized film showed lower moisture content than the glycerol-plasticized film, as it has the least number of hydroxyl groups and the lowest molecular weight compared with other plasticizers, it was

expected that EG-plasticized film absorbed more water than other films. Among the other samples tested, the moisture content decreased in the order: sucrose > mannitol > sorbitol > glucose > galactose > fructose > xylitol > PG. It was expected that the water uptake of the plasticizers increased by increasing hydroxyl group numbers, which strongly interact with water molecules by forming hydrogen bonds, but the results showed that the chances of plasticizers interacting with polymeric starch and guar chains are greater because their molecular structure is more similar to constituent units of polymers [42]. Another possible reason for this order could be owing to interactions between hydroxyl groups of starch and hydroxyl groups of plasticizers, which result in the lack of interactions sites for water in glucose monomers of polymers during drying [41]. For monosaccharide-plasticized films, although they had similar molecular weights, the moisture content of glucose-plasticised PSGG films was lower than that of corresponding films. Since glucose has more similar molecular structure to the molecular structure of glucose units in starch, it is conceivable that it shows better interactions with polymeric starch and guar gum chains. This means that glucose-containing films exhibited higher intermolecular forces and a lower capacity to interact with water [43].

It is useful to calculate the equilibrium moisture content of the films in a wide range of a_w due to the compatibility of the plasticizers and their hydrophilic nature [44]. The mean equilibrium moisture content (EMC) values of films are presented in Figure 1a, b. All the sorption isotherms slightly showed the Type II isotherm, which is an S type curve. It can be seen that the EMC increased with increasing a_w for each film. Water content of films increased linearly as a_w increased up to about 0.4 and then an upward curvature trend was detected above this a_w level. At $a_w < 0.4$, the equilibrium moisture content was found reducing by increasing in hydroxyl groups of plasticizers. Explanation for this trend is possibly strict prevention against water adsorption due to forming hydrogen bonds between

hydroxyl groups of biopolymer and plasticizers, as well as, low tendency of plasticizers to interact water at low water activities [41, 45, 46]. It has been proposed that sugar molecules stabilize the amorphous region of the starch granule by confining the mobility and flexibility of starch chains, hence longer sugar chains can bridge more starch chains than shorter chains [47]. Development of a bridge between starch chains and sugar molecules decreased water adsorption capacity depending on the concentration, type, size, and the flexibility of the polyhydroxy compounds [48]. On the contrary, as a_w increased, the uptake of water soared by increasing of number of hydroxyl groups in plasticizers. The hydrophilicity of film by exposing the hydroxyl groups of plasticizers improved, causing the polymeric structure unfastened and the free volume of the polymer increased, consequently, permitting more active sites to associate with water molecules [40, 42]. Besides, water uptakes at higher a_w accelerated, because the water–water interaction, which was much stronger than the starch–water interaction, became the driving force of the adsorption process on the surface of starch films [49].

The applied models presented good explanations of the moisture isotherms throughout the whole range of water activity. The values of GAB, Peleg and Ferro-Fontan models with the correlation coefficient (R^2) and the mean relative percentage deviation modulus (M_e) are shown in Table 4. The GAB equation properly fitted the experimental data since R^2 values of prediction for all samples were more than 0.99. The mean relative percentage deviation modulus (M_e), with a modulus value below 10% suggested a satisfactory fit for experimental values [50]. Comparing with PSGG film containing EG and maltitol, the monolayer moisture content varied from 39.337 to 12.638 g water/100 g dry solids. The values of other GAB equation parameters $0 \leq C \leq 2$ and $k < 1$ represents that isotherms are of Type II (sigmoid) [51]. The C values reduced considerably, signifying that the attaching strength of monolayer

water to the sorption sites in the blend films decreased as hydroxyl groups in plasticizer increased. Additionally, the plasticizer type did not affect parameter k .

3.6. Water solubility

The solubility of the PSGG films in water revealed significant differences regarding plasticizer type (Table 3). The solubility of the PSGG films increased by increasing plasticizer molecular weight and hydroxyl groups. Films with EG were less soluble than other films followed by films plasticized with PG, glycerol and glucose. The changes of glucose to connect with polymeric matrix chains are higher as it is more similar to the molecular structure of glucose units. Thus, the films comprising glucose have a high level of intermolecular forces and attractions within the matrix, bringing about a lower capability to interact with water and low solubility in comparison with other sugar-plasticized films. Maltitol plasticized films were the most soluble films in spite of the fact that these films presented the least equilibrium moisture content. This trend can be associated with increased content of hydrophilic groups in the final mass of the sample [4]. Moreover, this may propose that by increasing molecular weight, the plasticizers were not penetrated successfully between the polymer chains thus leaving the gaps from which they escaped easily in aqueous medium [15, 52]. This is also supported by higher moisture content of films in higher water activities.

3.7. Water vapor permeability

The WVP of plasticized films was found to be in the range of $1.609 \times 10^{-9} - 1.505 \times 10^{-9}$ ($\text{gm}^{-1} \text{s}^{-1} \text{Pa}^{-1}$) and was very dependent on the type of plasticizer in the following order: EG > PG > maltitol > glycerol > sucrose > mannitol > sorbitol > xylitol > fructose > galactose > glucose (Table 3). The water vapor transmission through a hydrophilic film is dependent on the diffusion rate and solubility of water molecules in the film matrix [53]. Among the

plasticized films, EG-plasticized and PG-plasticized films exhibited the highest WVP values due to their low molecular weight. They can simply permeate into the polymer matrix by disturbing the intermolecular interaction among polymer chains and therefore accelerate the free volume for migration of water and other molecules to film structure [24]. Different results were reported in the previous study where glycerol-plasticized films had the highest value of WVP [38]. However, film plasticized with glycerol exhibited higher WVP values than other sugar plasticized-films except maltitol films, due to differences in their hydrophilicity nature and accessibility of hydroxyl groups to interact with water by hydrogen bonds. So, water molecules can more easily interact with the surface of the films plasticized with glycerol (i.e., higher solubility) and more freely penetrate through the film structure (i.e., higher diffusivity) causing the increase in WVP [20]. While, in other sugar plasticized-films, cross-link formation between hydroxyl groups of sugar molecules with those on polymer molecular chains [54], led to less free volume left in the structure of films for water molecules to transport through [38]. Maltitol-plasticized films had relatively the same value of WVP as those of glycol films. Due to the largest molecular weight of maltitol, it could be described that it did not insert the network of polymers rapidly and simply to produce a strong film by decreasing intermolecular distance between the polymers, so there were more gaps for more water diffusion. Monosaccharide plasticized films showed less WVP compared with other plasticized films. The more structural compatibility of glucose with starch had more detrimental effect in reducing the free volume and the movements of starch chains. On the other hand, the previous studies demonstrated that the hydroxyl groups and axial or equatorial hydroxyl groups of sugar molecules show different impacts on physicochemical properties of starch [55, 56]. These sugars were more resistant to the penetration of water to film structure. There are two probable reasons for this performance: (1) reduction of the effective water by hydration of these molecules, which is equal to the effect of higher

concentration of starch in film formulation, (2) their interaction with polymer molecular chains stabilizes the crystalline region of starch [57]. Therefore, stabilization of the starch crystalline region led to reduction of WVP. Generally, the higher degree of crystallinity causes the lower permeability of a film [58, 59].

3.8. *Optical properties*

The results of transparency and color parameters of PSGG films with different plasticizers are tabulated in Table 5. Transparency value changed from 84.275 to 70.172 for the films containing EG and maltitol, respectively. The differences in transparency of films consist of different types of plasticizers might be owing to different molecular weight, composition, size, nature and some characteristics of plasticizers applied that might inhibit the light transmission through the films [60]. The transparency of films presented a reduction affinity, when molecular weight and hydroxyl group numbers increased ($p < 0.05$), probably due to formation crosslinks (sugar bridges) between polymer chains altering the refractive index and preventing the passage of the light through the film matrix [61]. Larger molecules can bridge longer gaps between polymer chains and accordingly create more crosslinks than smaller molecules [30]. The reduction of transparency may be attributed to the modified network structure by the crosslinks, which functions as a barrier to light. In addition, the thickness of films is another reason for decreasing transparency. Previous researches have reported a negative relationship between the thickness and transparency of the films [11, 62, 63].

Color is a fundamental feature in acceptability of biopolymer films and greatly depends on various factors including plasticizer incorporation, thermal treatment, manufacture technology, and condition of storage [64]. Films color parameters are characterized in Table 5 as Hunter system L (lightness), a (redness) and b (yellowness) values. The results showed an increase in ΔE values by incorporation of various plasticizers due to changes in L , a , and b

values of films. With increase in molecular weight and hydroxyl group numbers of plasticizers, b value (yellowness) of films increased, whereas L and a parameters decreased indicating increase in darkness and greenness of the films, respectively [11]. Increase in L value for gelatin and gum cordia based films plasticized with glycerol, sorbitol, ethylene glycol, PEG 200 and PEG 400 have been reported [44, 65]. The decrease in L parameter was in agreement with the transparency decrease in films. It has been proposed that reduction of moisture content changes the reflection of light at the film surface, leading to film samples to be more reddish (a values increased) [26, 66]. These observations are consistent with visual examination of the films representing a transparent and homogenous appearance for all film formulations.

3.9. Mechanical properties

The mechanical properties of the plasticized PSGG films at different RH including the tensile strength (TS), Young's modulus (YM) and elongation at break (E) are summarised in Table 6. The tensile mechanical properties showed a dependency to both RH and plasticizer type. It has been indicated that the configuration, molecular size, and total number of functional hydroxyl groups of the plasticizer along with its compatibility with the polymer could influence the mechanical properties of polymer films [67]. In general, TS and YM reduced as RH increased, while E exhibited the positive relation with RH, because the low molecular weight of water molecules produces a weak polymer matrix owing to an enhanced free volume and a large increase in molecular flexibility of amorphous and relatively crystalline polymers [19].

Over the lower range of RH ($RH \leq 0.43$), TS and YM increased as the molecular weight and numbers of hydroxyl group of plasticizer increased coinciding with a decrease in elongation at break, indicating an antiplasticizing effect of plasticizers. Within the plasticiser tested at

RH = 11%, PG-containing blend films presented significant lower TS values than other plasticised films ($P < 0.05$; Table. 6), while films plasticised with maltitol exhibited the highest TS values. This could be associated with the structural modifications of polymer network by incorporation of plasticizer. A greater number of hydroxyl groups in plasticizer increases the interaction between the carboxyl groups of starch and guar gum, decreasing movement between the chains of starch and guar gum as well as reducing the interaction with water, which is the natural plasticizer for carbohydrate films [4]. Therefore, the matrix of the film becomes more dense, preventing motions of polymer chains under stress, hence increasing the film resistance [68]. The mechanical characteristics of films are mainly related to arrangement, and orientation of polymer chains in the network which depend on allocation and density of intermolecular and intra-molecular interactions [69]. Another factor to be deliberated could be retrogradation process and the water-induced crystallization of the biopolymer films [70]. At very low and intermediate RH, the development of crystallites in the starch films promoted the antiplasticization effect [71]. Applying force during test induced the movement or vibration of the starch polymer chains, which caused separation of water and plasticizer molecules from polymer chains. The larger plasticizer molecule, the easier it pushed aside. Under such conditions, D-glucosyl residues of the amylose or amylopectin interacted to form strong hydrogen bonds prompting retrogradation or recrystallization [49, 70, 72, 73]. Another probable reason could also be “hole filling” theory for antiplasticization of polymers by diluents at low RH [72, 74, 75]. In the polymeric system, “holes” are created by increasing rearrangement of polymer chains and free volume as a result of development of much greater bond breaking/forming under stress [72]. Therefore, TS and YM showed an increase due to filling “holes”, reducing “hole free volume” and further increasing structural orientation by water molecules in small amounts [20].

Above the higher RH ($\geq 65\%$), the TS and YM of all films decreased with increasing the molecular weight and numbers of hydroxyl group of plasticizers. As shown in sorption isotherm of films, plasticizers with higher numbers of hydroxyl group readily takes up water at $a_w \geq 0.4$, causing a plasticizing impact acting as a mobility enhancer and loss of film plasticity. There was an apparent synergistic effect between plasticizers and water at intermediate RH, signifying that films with plasticizer in the presence of high level of water performed mechanically as films with larger amount of plasticizers (with lower tensile strength and higher elongation) [76]. Generally, plasticizers apply a “blocking effect” by reducing the direct interactions (intra and intermolecular) among the polymer macromolecules and simultaneously creating more free volume between the polymers [17, 77]. So, less dense film structure causes less resistant to force and more flexible film. At RH = 84%, quantity of hydrogen bonds between starch-plasticizer and starch-starch reduced and more hydrogen bonds were generated between starch-water and polyol-water [45]. Consequently, the plastic effect of water and extension of pores and cracks resulting in film swelling and reduction of the E value due to the over-plasticization of the polymers [78]. In addition, reduced E could also be derived from increased starch crystallinity owing to high storage RH as has been described to happen in starch films [79, 80]. The films plasticized with glycerol showed the highest E value at higher RH. The small size of glycerol molecule and its hygroscopic behavior improve its efficiency as a plasticizer and brought about greater plasticization influence than other plasticizers at an equal mass content [8].

The maximum puncture force and deformation of PSGG films at RH = 65% are seen in Figure 2. The results revealed that the puncture force and deformation were affected by plasticizer type. Increasing the molecular weight and numbers of hydroxyl group of plasticizers decreased the maximum puncture force of film. The lowest puncture force (10.460 N) and the highest puncture deformation (7.143 mm) values were obtained for films

formulated with maltitol and glycerol, respectively. The maximum puncture force of EG-plasticized films was significantly higher than those of others, although it showed similar puncture deformation compared to other plasticizers. Glycols used in this study, were similar in structure and shape, however, EG is lower in size thus interact more efficiently with polymers than of PG. The small size of EG produced more direct interaction between polymer molecules resulting in high intermolecular cohesive force [38] and high puncture force. Compared with EG-plasticized films, films plasticized with glycerol presented much lower values of puncture force, and much higher puncture deformation, although they (glycerol and EG) are almost similar in molecule size and structure. This may be due to higher affinity to moisture and plasticizing effectiveness of glycerol. Monosaccharide-plasticized films had lower or same puncture force and puncture deformation values than sorbitol and mannitol plasticized films, representing that monosaccharides had good plasticizing effect in comparison with common polyols in the same molar ratio concentration. However, the lowest puncture force of films containing fructose compared to those of other monosaccharide-plasticized films suggested that fructose developed weakest interaction with polymers. The xylitol films showed higher puncture deformation than films plasticized with sorbitol. These results might be described by the ring structure of sorbitol that restricts its capability to decrease hydrogen bonding between pea starch and guar gum chains [67]. On the other hand, the small size of xylitol molecule enhanced its efficiency as a plasticizer and determined its better plasticization influence than sorbitol at an equivalent mass content [8]. Sucrose films showed significantly lower values for puncture force and puncture deformation than other plasticized films, except maltitol. The bulky rings of α -D-glucose and β -D-fructose that constitute sucrose molecules, compared with straight chains of other plasticizers, reduce plasticization behavior of sucrose [18]. It has been previously declared that plasticizers with big molecular size showed less plasticizing effect [15, 52].

3.10. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was carried out to examine the microstructural view of the surface of PSGG films with different plasticizers. A microstructural study of the films provides a relationship between molecular orientation in the matrix and physicochemical characteristics of films [81]. The PSGG film without plasticizer (Figure 3) showed a less compact structure, with large pores and cracks, which is in good agreement with the results of preliminary visual examination. The rough and heterogeneous morphology of the films with PEG-400 confirmed its incompatibility with PSGG, and consequently it migrated out from the polymer matrix because of phase separation between PSGG and PEG-400. Micrographs of the film surfaces, at a magnification of 1000 \times , showed distinguishable differences between the films containing different plasticizers. The films presented surfaces without cracks, breaks, or openings which are indicator of the miscibility and compatibility of employed plasticizers with PSGG films (Figure 4). The films containing low molecular weight plasticizer showed a more compact, homogenous, uniform and denser structure when compared with the films with high molecular weight plasticizers. Plasticized films displayed some irregular particles distributed uniformly along the network, which could be attributed to the swollen starch granule and its remnants.

3.11. Fourier-transform infrared (FTIR) spectroscopy

FTIR spectrums of PSGG films with different plasticizers are shown in Figure 5. The entire spectrum is very similar for all plasticized films and representing a common alcohol and hydroxy compound group frequencies [82]. FTIR assignment of PSGG films consisted of the following frequencies. The broad band between 3000 and 3700 cm^{-1} was associated with the complex vibrational stretches attributed by the free, inter- and intramolecular bound hydroxyl groups between neighbouring molecules constituting the main conformation of starch [38,

82]. The sharp peak at 2924 cm^{-1} was characteristic of C–H stretching (CH_2) [83]. The peak appearing at 1641 cm^{-1} was related to the strongly bound water exist in the starch [38] owing to the hygroscopic behavior of starch [1]. The peaks at 1409 and 1433 cm^{-1} were related to the C–H bending of CH_2 . Peaks at 1240 , 1299 , and 1333 cm^{-1} were attributed to O–H bending because of the primary or secondary alcohols [82]. Variations in structure and crystallinity were occurred in the area between 1200 and 950 cm^{-1} , which is the fingerprinting region distinctive for a molecule [1, 84-86]. There were three typical bands between 990 cm^{-1} and 1160 cm^{-1} , associated with C–O bond stretching. The bands at around 1150 cm^{-1} and 1080 cm^{-1} were representative of C–O–H in film structure, whereas the band between 994 cm^{-1} and 1077 cm^{-1} displayed the anhydroglucose ring O–C stretch [8, 38, 87, 88]. The band at around 930 cm^{-1} was characteristic of the glycosidic linkages [89]. The peak at 1000 cm^{-1} was related to water sensitivity and was recognized as intramolecular hydrogen bonding of hydroxyl groups [90] or plasticizing effect of water [1, 38, 88].

Figure 5A exhibits the spectra of the EG-, PG- and glycerol-plasticized films. Their molecules presented similar effect to the structure of molecules in PSGG films. Within the O–H stretching region, the EG-plasticized film showed the highest wavenumber, due to its smallest molecular weight, it can efficiently decrease the interaction between the starch polymers. Figure 5B illustrates the FTIR spectra of monosaccharide and disaccharide plasticized films. The most obvious change in FTIR spectrum was observed in glucose plasticized films. Figure 5C demonstrated the spectra of the polyol-plasticized films. It was difficult to find any difference between the spectra of the sorbitol- and maltitol-plasticized films. The similar results had been suggested by Zhang and Han [38]. Generally, the shift of a peak at 3369 cm^{-1} to 3248 cm^{-1} for EG-plasticized and maltitol-plasticized films, respectively, suggested an increase of intermolecular hydrogen bonding and anti-plasticization effect by increasing the hydroxyl groups in plasticizers. This indicates that all the hydroxyl groups in

the polymer contributed to hydroxyl group of the plasticizer causing the substitution of polymer-polymer interaction to polymer-plasticizer interaction [15] and more new hydroxyl groups were involved in the hydrogen bonds with polymers [38]. The shift to lower wave numbers suggested a strong formation of hydrogen bonds (cross-links) within film [1]. These results were in agreement with other observed results in this study. In sucrose- and maltitol-plasticized films FTIR spectra, a phase separation can be seen due to their higher molecular weight. This shift appears to imply that the incorporation of sucrose and maltitol may inhibit the improvement of hydrogen bonding during the drying process as they remain and solvate between the film polymeric chains [1, 83].

4. Conclusion

A new biocomposite edible film based on pea starch and guar gum was prepared and the influence of different plasticizers (glycols, sugars, and polyols) on functional properties of PSGG film was investigated. Pea starch/guar gum solution containing different plasticizers (25% w/w of film dry basis), except PEG-400, formed good flexible films. The functional properties of the films were changed according to the type of plasticizer. Incorporation of plasticizers in a_w lower than 0.4 significantly decreased water adsorption capacity and monolayer water content of the films due to cross-linking effect, but in a_w higher than 0.4, the films performed as hydrogel materials and increased moisture content as the molecular weight and number of hydroxyl groups of plasticizers increased. The shift of a peak at the O–H stretching region to lower wave numbers exhibited an increase of intermolecular hydrogen bonding and phase separation, especially by incorporation of sucrose and maltitol. It was shown that the PSGG films containing glycerol impart the highest flexibility under intermediate and higher RH. Moreover, it was proposed that monosaccharides have a great potential to be used as plasticizer because they showed a comparable characteristics with

other common used polyols in terms of mechanical, barrier and optical properties. Future researches on calculating the optimal amount and ratio of PEG-400 in mixture with other plasticizers using the response surface methodology is suggested to provide further perception into the plasticizing efficiency of PEG-400. In addition, further structural polymer chemistry for study the condition of homogeneous distribution of plasticizers and starch without phase separation, will be of great interest.

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Conflict of Interest

The authors declare no conflict of interest.

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Figure captions

Fig. 1a. Equilibrium moisture sorption isotherm of PSGG film with different plasticizers (w/w) at 25 °C. The symbols are experimental data and the lines are from the equations obtained by fitting the experimental data to GAB equation.

Fig. 1b. Equilibrium moisture sorption isotherm of PSGG film with different plasticizers (w/w) at 25 °C. The symbols are experimental data and the lines are from the equations obtained by fitting the experimental data to GAB equation.

Fig. 2. Puncture mechanical properties of PSGG films with different plasticizers.

Fig. 3. Micrographs of the PSGG film without plasticizer (1000 ×).

Fig. 4. Micrographs of the PSGG films (1000 ×). A: surface of with EG; B: surface of with PG; C: surface of with glycerol; D: surface of with xylitol; E: surface of with glucose; F: surface of with fructose; G: surface of with galactose; H: surface of with sorbitol; I: surface of with mannitol; J: surface of with sucrose; K: surface of with malitol; L: surface of with PEG-400.

Fig. 5. FTIR spectra of PSGG films containing different plasticizers in the region 400-4000 cm^{-1} .

Table 1. Plasticizers selected for study and their characteristics.*

| Plasticizer | Formula | Chain shape | Molecular weight (g/mol) | Number of hydroxyl groups | concentration | |
|-------------------------------|---|-------------|--------------------------|---------------------------|--------------------|----------------------|
| | | | | | g/100 g dry matter | mol/100 g dry matter |
| Ethylene glycol (EG) | C ₂ H ₆ O ₂ | Straight | 62.07 | 2 | 25 | 0.403 |
| Propylene glycol (PG) | C ₃ H ₈ O ₂ | Straight | 76.10 | 2 | 25 | 0.328 |
| Glycerol | C ₃ H ₈ O ₃ | Straight | 92.09 | 3 | 25 | 0.271 |
| Xylitol | C ₅ H ₁₂ O ₅ | Straight | 152.15 | 5 | 25 | 0.164 |
| Glucose | C ₆ H ₁₂ O ₆ | Ring | 180.16 | 5 | 25 | 0.139 |
| Fructose | C ₆ H ₁₂ O ₆ | Ring | 180.16 | 5 | 25 | 0.139 |
| Galactose | C ₆ H ₁₂ O ₆ | Ring | 180.16 | 5 | 25 | 0.139 |
| Sorbitol | C ₆ H ₁₄ O ₆ | Straight | 182.17 | 6 | 25 | 0.137 |
| Mannitol | C ₆ H ₁₄ O ₆ | Straight | 182.17 | 6 | 25 | 0.137 |
| Sucrose | C ₁₂ H ₂₂ O ₁₁ | Ring | 342.30 | 8 | 25 | 0.073 |
| Maltitol | C ₁₂ H ₂₄ O ₁₁ | Ring | 344.31 | 9 | 25 | 0.072 |
| Polyethylene glycol (PEG-400) | H(OCH ₂ -CH ₂) ₈ OH | Straight | 400 | 2 | 25 | 0.062 |

* Adopted from Galdeano et al. [19] and Antoniou et al. [52].

Table 2. Swelling power and solubility index of film suspensions with and without plasticizers (w/w) at different temperatures.

| Swelling power | Temperature (°C) | | | |
|----------------|------------------------------|-----------------------------|------------------------------|------------------------------|
| | 60 | 70 | 80 | 90 |
| EG | 3.152±0.094 ^{Dd} | 5.867±0.432 ^{Ce} | 12.990±0.432 ^{B,de} | 17.437±1.421 ^{Ad} |
| PG | 3.815±0.562 ^{Dc} | 6.710±0.460 ^{Cd} | 13.826±0.456 ^{Bd} | 18.830±0.924 ^{Ac} |
| Glycerol | 2.758±0.253 ^{D,de} | 5.254±0.724 ^{C,ef} | 12.343±0.738 ^{B,ef} | 16.681±0.225 ^{A,de} |
| Xylitol | 2.362±0.354 ^{D,ef} | 4.779±0.404 ^{C,fg} | 11.911±0.397 ^{Bf} | 15.916±0.484 ^{A,ef} |
| Glucose | 1.329±0.154 ^{D,hi} | 3.262±0.095 ^{Ci} | 10.352±0.106 ^{Bh} | 13.356±0.538 ^{A,gh} |
| Fructose | 1.979±0.022 ^{D,fg} | 4.389±0.520 ^{C,gh} | 11.512±0.520 ^{B,fg} | 15.283±0.499 ^{Af} |
| Galactose | 1.580±0.186 ^{D,gh} | 3.785±0.103 ^{C,hi} | 10.908±0.103 ^{B,gh} | 14.579±0.103 ^{A,fg} |
| Sorbitol | 1.093±0.078 ^{D,hij} | 2.540±0.335 ^{Cj} | 9.363±0.335 ^{Bi} | 12.701±0.426 ^{A,hi} |
| Mannitol | 0.929±0.088 ^{C,ij} | 1.848±0.063 ^{C,jk} | 8.305±0.631 ^{Bj} | 12.109±1.346 ^{A,hi} |
| Sucrose | 0.559±0.048 ^{C,jk} | 1.428±0.258 ^{C,kl} | 7.818±0.768 ^{Bj} | 11.656±0.564 ^{A,ij} |
| Maltitol | 0.165±0.041 ^{Dk} | 1.084±0.109 ^{Cl} | 6.540±0.621 ^{Bk} | 10.545±0.552 ^{Aj} |
| PEG-400 | 6.804±0.783 ^{Da} | 11.056±0.683 ^{Ca} | 18.179±0.683 ^{Ba} | 24.333±1.157 ^{Aa} |
| PSGG | 4.252±0.539 ^{Dc} | 7.907±0.552 ^{Cc} | 14.697±0.156 ^{Bc} | 19.535±0.442 ^{Ac} |
| PS | 5.469±0.363 ^{Db} | 9.315±0.495 ^{Cb} | 16.438±0.495 ^{Bb} | 21.576±0.770 ^{Ab} |

| Solubility index | Temperature (°C) | | | |
|------------------|-----------------------------|------------------------------|--------------------------------|------------------------------|
| | 60 | 70 | 80 | 90 |
| EG | 3.267±0.156 ^{Dd} | 5.760±0.359 ^{C,de} | 12.830±0.330 ^{B,cd} | 20.192±0.330 ^{Ad} |
| PG | 3.803±0.088 ^{Dc} | 6.072±0.453 ^{C,cd} | 13.675±0.453 ^{Bc} | 21.132±0.511 ^{A,cd} |
| Glycerol | 2.844±0.374 ^{De} | 5.468±0.527 ^{C,def} | 12.004±0.672 ^{B,df} | 18.540±0.747 ^{Ae} |
| Xylitol | 2.415±0.305 ^{Df} | 5.071±0.053 ^{C,efg} | 11.473±0.579 ^{B,def} | 17.904±0.579 ^{A,ef} |
| Glucose | 1.514±0.191 ^{D,hi} | 3.882±0.436 ^{C,hi} | 9.652±0.906 ^{B,gh} | 15.746±0.870 ^{A,gh} |
| Fructose | 2.051±0.187 ^{D,fg} | 4.854±0.109 ^{C,fg} | 10.957±0.508 ^{B,efg} | 17.241±0.508 ^{A,ef} |
| Galactose | 1.885±0.253 ^{D,gh} | 4.389±0.366 ^{C,gh} | 10.125±1.423 ^{B, fgh} | 16.756±1.423 ^{A,fg} |
| Sorbitol | 1.143±0.033 ^{D,ij} | 3.259±0.124 ^{C,ij} | 8.869±0.122 ^{B,hi} | 14.710±0.122 ^{A,hi} |
| Mannitol | 0.929±0.072 ^{Cj} | 2.759±0.588 ^{C,jk} | 8.195±1.561 ^{Bi} | 13.930±1.352 ^{A,ij} |
| Sucrose | 0.422±0.212 ^{Dk} | 2.159±0.204 ^{C,kl} | 7.718±0.128 ^{Bi} | 12.839±0.173 ^{Aj} |
| Maltitol | 0.104±0.089 ^{Dk} | 1.626±0.353 ^{Cl} | 6.185±0.401 ^{Bj} | 11.358±0.925 ^{Ak} |
| PEG-400 | 5.917±0.339 ^{Da} | 9.250±0.543 ^{Ca} | 17.520±1.319 ^{Ba} | 26.251±1.319 ^{Aa} |
| PSGG | 3.952±0.244 ^{D,bc} | 6.441±0.408 ^{C,bc} | 14.044±0.408 ^{B,bc} | 22.110±0.628 ^{A,bc} |
| PS | 4.369±0.502 ^{Db} | 7.062±0.770 ^{Cb} | 15.107±0.717 ^{Bb} | 23.159±0.687 ^{Ab} |

* Values are the average of triplicates ± standard deviation. Means at same column with different lower case are significantly different ($P < 0.05$); means at same row with different upper case are significantly different ($P < 0.05$).

Table 3. Effect of different plasticizers on physical properties of PSGG films.*

| Plasticizers | Apparent Viscosity (mPa.s) | Thickness $\times 10^{-3}$ (m) | Density $\times 10^{-3}$ (gmm ⁻³) | Moisture Content (%) | Solubility in water (%) | WVP $\times 10^{-9}$ (gs ⁻¹ m ⁻¹ Pa ⁻¹) |
|--------------|-----------------------------------|-----------------------------------|--|-----------------------------------|-----------------------------------|--|
| EG | 135.958 \pm 9.404 ^k | 0.094 \pm 0.007 ⁱ | 1.312 \pm 0.109 ^g | 19.094 \pm 0.933 ^b | 21.810 \pm 1.951 ⁱ | 1.609 \pm 0.087 ^a |
| PG | 167.175 \pm 11.048 ^j | 0.112 \pm 0.007 ^h | 1.574 \pm 0.203 ^f | 18.207 \pm 0.227 ^{bc} | 24.777 \pm 1.063 ^{hi} | 1.510 \pm 0.0575 ^b |
| Glycerol | 192.347 \pm 2.800 ^j | 0.126 \pm 0.002 ^g | 1.758 \pm 0.152 ^{ef} | 21.166 \pm 0.604 ^a | 27.677 \pm 1.191 ^{fgh} | 1.397 \pm 0.321 ^{cd} |
| Xylitol | 261.402 \pm 12.066 ⁱ | 0.134 \pm 0.004 ^g | 1.978 \pm 0.301 ^d | 17.684 \pm 0.484 ^{bcd} | 29.643 \pm 1.122 ^{efg} | 1.262 \pm 0.177 ^{fg} |
| Glucose | 301.552 \pm 19.048 ^h | 0.144 \pm 0.003 ^f | 2.114 \pm 0.732 ^{cd} | 15.115 \pm 0.726 ^{ef} | 26.510 \pm 0.787 ^{gh} | 1.133 \pm 0.110 ⁱ |
| Fructose | 368.219 \pm 24.720 ^g | 0.161 \pm 0.007 ^e | 1.951 \pm 0.845 ^{de} | 17.050 \pm 0.731 ^{cd} | 32.610 \pm 1.487 ^{cdf} | 1.222 \pm 0.104 ^{gh} |
| Galactose | 351.552 \pm 24.812 ^g | 0.152 \pm 0.005 ^{ef} | 2.110 \pm 0.882 ^{cd} | 16.484 \pm 1.101 ^{df} | 31.177 \pm 1.671 ^{dfg} | 1.192 \pm 0.098 ^h |
| Sorbitol | 415.192 \pm 7.453 ^f | 0.172 \pm 0.004 ^d | 2.212 \pm 0.166 ^c | 14.332 \pm 1.127 ^{fg} | 34.010 \pm 1.663 ^{cd} | 1.304 \pm 0.230 ^{ef} |
| Mannitol | 454.331 \pm 27.522 ^e | 0.184 \pm 0.005 ^c | 2.506 \pm 1.745 ^b | 13.617 \pm 1.183 ^{fg} | 35.843 \pm 0.941 ^{bc} | 1.347 \pm 0.091 ^{de} |
| Sucrose | 552.960 \pm 24.811 ^d | 0.194 \pm 0.004 ^b | 2.800 \pm 0.123 ^a | 12.817 \pm 1.186 ^g | 38.277 \pm 2.463 ^b | 1.407 \pm 0.200 ^c |
| Maltitol | 676.294 \pm 15.259 ^c | 0.206 \pm 0.011 ^a | 2.993 \pm 0.802 ^a | 10.382 \pm 0.630 ^h | 44.610 \pm 4.515 ^a | 1.505 \pm 0.763 ^b |
| PEG-400 | 937.012 \pm 15.215 ^a | - | - | - | - | - |
| PSGG | 833.679 \pm 20.432 ^b | - | - | - | - | - |

* Values are the means of triplicates \pm standard deviations. Means at same line with different super manuscript letters are significantly different ($P < 0.05$).

Table 4. Estimated model constants and values of coefficients and mean relative percentage deviation moduli for PSGG films with different plasticizers at 25 °C.

| Model constants | | plasticizers | | | | | | | | | | |
|-----------------------------|--------------|--------------|--------|----------|---------|---------|----------|-----------|----------|----------|---------|----------|
| | | EG | PG | Glycerol | Xylitol | Glucose | Fructose | Galactose | Sorbitol | Mannitol | Sucrose | Maltitol |
| GAB (0.11-0.96) | m_0 (%) | 39.337 | 35.989 | 49.829 | 29.879 | 20.687 | 28.815 | 25.918 | 22.884 | 20.197 | 15.529 | 12.638 |
| | C | 0.749 | 0.620 | 1.442 | 0.728 | 0.697 | 0.712 | 0.699 | 0.671 | 0.666 | 0.665 | 0.655 |
| | K | 0.928 | 0.956 | 1.087 | 0.989 | 1.296 | 1.200 | 1.150 | 1.145 | 0.901 | 1.695 | 1.180 |
| | M_e | 5.492 | 7.928 | 6.356 | 4.742 | 5.153 | 4.886 | 4.854 | 6.442 | 9.354 | 9.726 | 7.395 |
| | R^2 | 0.995 | 0.995 | 0.997 | 0.997 | 0.999 | 0.997 | 0.999 | 0.994 | 0.984 | 0.994 | 0.993 |
| PELEG (0.11-0.96) | k_1 | 85.404 | 86.144 | 83.001 | 87.587 | 94.133 | 88.945 | 93.321 | 99.330 | 103.904 | 117.023 | 122.689 |
| | k_2 | 23.768 | 20.933 | 25.465 | 19.156 | 13.274 | 20.631 | 17.415 | 18.951 | 16.683 | 12.237 | 11.842 |
| | n_1 | 1.510 | 1.199 | 1.556 | 1.796 | 2.072 | 1.963 | 2.076 | 1.784 | 1.818 | 1.812 | 1.935 |
| | n_2 | 82.371 | 82.433 | 85.431 | 83.342 | 81.761 | 81.532 | 80.433 | 78.414 | 75.352 | 72.439 | 71.440 |
| | M_e | 3.674 | 4.088 | 8.022 | 10.741 | 11.802 | 11.327 | 12.323 | 8.402 | 10.725 | 10.164 | 11.845 |
| | R^2 | 0.995 | 0.997 | 0.995 | 0.995 | 0.997 | 0.994 | 0.995 | 0.994 | 0.994 | 0.995 | 0.995 |
| Ferro-Fontan (0.11-0.96) | γ | 7.235 | 5.420 | 7.690 | 5.332 | 4.530 | 4.946 | 4.676 | 5.967 | 6.919 | 6.919 | 6.022 |
| | α | 2.957 | 2.362 | 42.279 | 4.754 | 3.584 | 3.626 | 2.576 | 6.276 | 7.276 | 7.276 | 7.895 |
| | r | 0.369 | 0.404 | 0.150 | 0.270 | 0.279 | 0.289 | 0.344 | 0.119 | 0.126 | 0.126 | 0.113 |
| | M_e | 4.528 | 5.399 | 6.340 | 4.279 | 4.890 | 4.415 | 4.195 | 7.516 | 10.050 | 10.342 | 13.199 |
| | R^2 | 0.995 | 0.996 | 0.995 | 0.997 | 0.999 | 0.997 | 0.999 | 0.994 | 0.993 | 0.994 | 0.994 |

Table 5. Effect of different plasticizers on optical properties of PSGG films.*

| Plasticizers | <i>L</i> | <i>a</i> | <i>b</i> | ΔE | Transparency (%) |
|--------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| EG | 95.329±0.576 ^a | -2.756±0.065 ^a | 5.090±0.526 ^f | 2.146±0.586 ^f | 84.275±0.628 ^a |
| PG | 94.495±0.481 ^a | -3.242±0.085 ^{ab} | 5.723±0.411 ^f | 2.832±0.484 ^f | 83.875±0.878 ^{ab} |
| Glycerol | 93.734±1.978 ^a | -3.816±0.100 ^{bc} | 6.833±0.931 ^e | 3.952±1.872 ^f | 82.275±1.623 ^b |
| Xylitol | 90.662±0.581 ^b | -4.037±0.081 ^c | 7.566±0.505 ^{de} | 6.991±0.690 ^e | 80.159±0.748 ^c |
| Glucose | 85.629±1.160 ^d | -5.111±0.188 ^d | 8.700±0.345 ^{abc} | 9.712±0.883 ^d | 74.305±0.894 ^f |
| Fructose | 87.995±0.964 ^c | -4.737±0.097 ^d | 7.933±0.407 ^{cd} | 12.222±1.120 ^c | 78.505±0.751 ^{cd} |
| Galactose | 86.240±1.004 ^{cd} | -4.911±0.767 ^d | 8.200±0.146 ^{bcd} | 11.491±1.022 ^{cd} | 76.738±2.065 ^{de} |
| Sorbitol | 85.335±2.057 ^d | -6.282±0.630 ^e | 8.500±0.460 ^{abc} | 12.684±1.853 ^c | 75.105±0.416 ^{ef} |
| Mannitol | 84.502±0.586 ^{de} | -6.616±0.613 ^{ef} | 8.833±0.167 ^{ab} | 13.600±0.547 ^{bc} | 73.305±1.165 ^f |
| Sucrose | 82.995±1.762 ^{ef} | -6.982±0.111 ^{fg} | 8.983±0.210 ^{ab} | 15.142±1.596 ^{ab} | 71.171±1.038 ^g |
| Maltitol | 81.335±0.991 ^f | -7.334±0.064 ^g | 9.227±0.165 ^a | 16.837±0.957 ^a | 70.171±0.373 ^g |

* Values are the means of triplicates \pm standard deviations. Means at same line with different super manuscript letters are significantly different ($P < 0.05$).

Table 6. Tensile mechanical properties of PSGG films with different plasticizers.*

| Tensile strength (MPa) | RH% | | | |
|------------------------------------|---------------------------------|---------------------------------|----------------------------------|-------------------------------|
| | 11.3 | 43.2 | 65.4 | 84.3 |
| EG | 33.542±1.062 ^{A,fg} | 27.901±1.161 ^{B,fg} | 34.768±3.643 ^{Aa} | 23.486±1.016 ^{Ca} |
| PG | 31.434±0.777 ^{Ag} | 26.821±1.189 ^{Bg} | 30.409±1.022 ^{Ab} | 21.975±1.158 ^{Cb} |
| Glycerol | 35.383±0.740 ^{Af} | 30.768±3.024 ^{B,ef} | 26.665±1.751 ^{Cc} | 19.147±1.460 ^{Dc} |
| Xylitol | 36.306±2.786 ^{Af} | 31.616±1.096 ^{Be} | 23.486±2.335 ^{Cd} | 17.434±0.686 ^{Dd} |
| Glucose | 45.152±2.161 ^{A,cd} | 38.098±1.451 ^{B,cd} | 20.024±1.442 ^{Ce} | 14.852±0.716 ^{De} |
| Fructose | 40.793±1.768 ^{Ae} | 34.927±0.512 ^{Bd} | 17.716±1.768 ^{Ce} | 13.115±0.328 ^{D,fg} |
| Galactose | 43.742±2.138 ^{Ad} | 36.098±0.922 ^{Bd} | 18.870±0.972 ^{Ce} | 13.998±0.092 ^{D,ef} |
| Sorbitol | 46.578±2.071 ^{A,cd} | 39.722±4.181 ^{B,bc} | 20.922±0.814 ^{C,de} | 16.550±0.864 ^{Cd} |
| Mannitol | 47.283±0.369 ^{A,bc} | 41.194±0.910 ^{B,bc} | 20.616±1.128 ^{C,de} | 13.822±0.524 ^{D,ef} |
| Sucrose | 49.870±1.555 ^{A,ab} | 42.929±0.822 ^{B,ab} | 18.332±2.101 ^{Ce} | 12.068±0.693 ^{Dg} |
| Maltitol | 52.639±0.975 ^{Aa} | 45.396±1.128 ^{Ba} | 14.434±1.066 ^{Cf} | 9.955±0.523 ^{Dg} |
| Percent elongation at break (%) | RH% | | | |
| | 11.3 | 43.2 | 65.4 | 84.3 |
| EG | 13.715±1.531 ^{Aa} | 14.715±0.917 ^{Aa} | 10.799±1.541 ^{B,def} | 9.132±1.173 ^{B,ef} |
| PG | 12.465±0.723 ^{A,ab} | 13.611±1.639 ^{Aa} | 13.299±0.962 ^{A,bcd} | 11.440±0.916 ^{A,bcd} |
| Glycerol | 11.632±0.833 ^{Bb} | 15.585±0.772 ^{Aa} | 17.049±2.423 ^{Aa} | 14.502±1.786 ^{AB,a} |
| Xylitol | 9.549±0.596 ^{Cc} | 11.549±1.190 ^{BC,b} | 14.549±1.959 ^{A,abc} | 12.370±0.784 ^{AB,bc} |
| Glucose | 6.465±1.115 ^{C,defg} | 7.965±0.503 ^{BC,cde} | 11.761±1.454 ^{A,cde} | 9.549±1.235 ^{B,def} |
| Fructose | 8.215±0.787 ^{B,cd} | 9.465±1.929 ^{Bc} | 14.049±2.230 ^{A,abc} | 11.002±0.686 ^{B,cde} |
| Galactose | 7.844±0.295 ^{C,cde} | 8.511±0.989 ^{BC,cd} | 13.677±1.734 ^{A,bcd} | 10.177±0.913 ^{B,de} |
| Sorbitol | 6.632±1.840 ^{B,def} | 7.615±1.924 ^{B,cde} | 15.382±2.477 ^{A,ab} | 13.448±1.190 ^{A,ab} |
| Mannitol | 6.011±0.989 ^{C,efg} | 6.700±0.88 ^{C,de} | 13.677±1.373 ^{A,bcd} | 11.177±1.272 ^{B,cde} |
| Sucrose | 5.407±0.187 ^{B,fg} | 6.022±0.668 ^{Be} | 10.049±0.370 ^{A,ef} | 9.215±1.269 ^{A,ef} |
| Maltitol | 4.549±1.533 ^{Cg} | 5.834±0.213 ^{BC,e} | 8.465±0.665 ^{Af} | 7.569±0.900 ^{AB,f} |
| Young modulus (MPa) | RH% | | | |
| | 11.3 | 43.2 | 65.4 | 84.3 |
| EG | 246.115±20.919 ^{Be} | 190.425±19.992 ^{Cg} | 323.145±13.526 ^{Aa} | 260.247±36.744 ^{Ba} |
| PG | 252.504±8.706 ^{Ae} | 199.652±32.739 ^{Bg} | 229.498±19.333 ^{AB,b} | 193.210±23.166 ^{Bb} |
| Glycerol | 305.182±21.504 ^{Ae} | 197.366±15.266 ^{Bg} | 159.212±30.117 ^{BC,cde} | 134.005±24.287 ^{Cc} |
| Xylitol | 380.936±33.979 ^{A,de} | 276.087±35.202 ^{B,fg} | 161.937±6.097 ^{C,cd} | 141.554±14.394 ^{Cc} |
| Glucose | 708.063±85.888 ^{A,bcd} | 480.200±45.990 ^{B,de} | 171.022±9.439 ^{C,cd} | 156.900±16.360 ^{Cc} |
| Fructose | 498.218±27.266 ^{A,cde} | 379.823±80.148 ^{B,ef} | 126.929±9.344 ^{Ce} | 119.516±7.925 ^{Cc} |
| Galactose | 558.609±44.060 ^{A,cde} | 428.384±55.739 ^{B,de} | 139.077±14.701 ^{C,de} | 138.275±12.226 ^{Cc} |
| Sorbitol | 733.345±173.985 ^{A,bc} | 537.580±111.095 ^{B,cd} | 138.070±19.824 ^{C,de} | 123.676±12.402 ^{Cc} |
| Mannitol | 800.630±128.198 ^{A,bc} | 623.978±103.805 ^{B,bc} | 151.247±8.835 ^{C,cde} | 124.658±14.277 ^{Cc} |
| Sucrose | 923.585±56.979 ^{Ab} | 719.300±86.546 ^{B,ab} | 182.480±20.068 ^{Cc} | 132.002±11.509 ^{Cc} |
| Maltitol | 1281.681±554.439 ^{Aa} | 778.851±34.044 ^{Aa} | 171.810±25.141 ^{B,cd} | 133.309±22.883 ^{Bc} |

* Values are the average of triplicates ± standard deviation. Means at same row with different upper case are significantly different ($P < 0.05$); means at same column with different lower case are significantly different ($P < 0.05$).

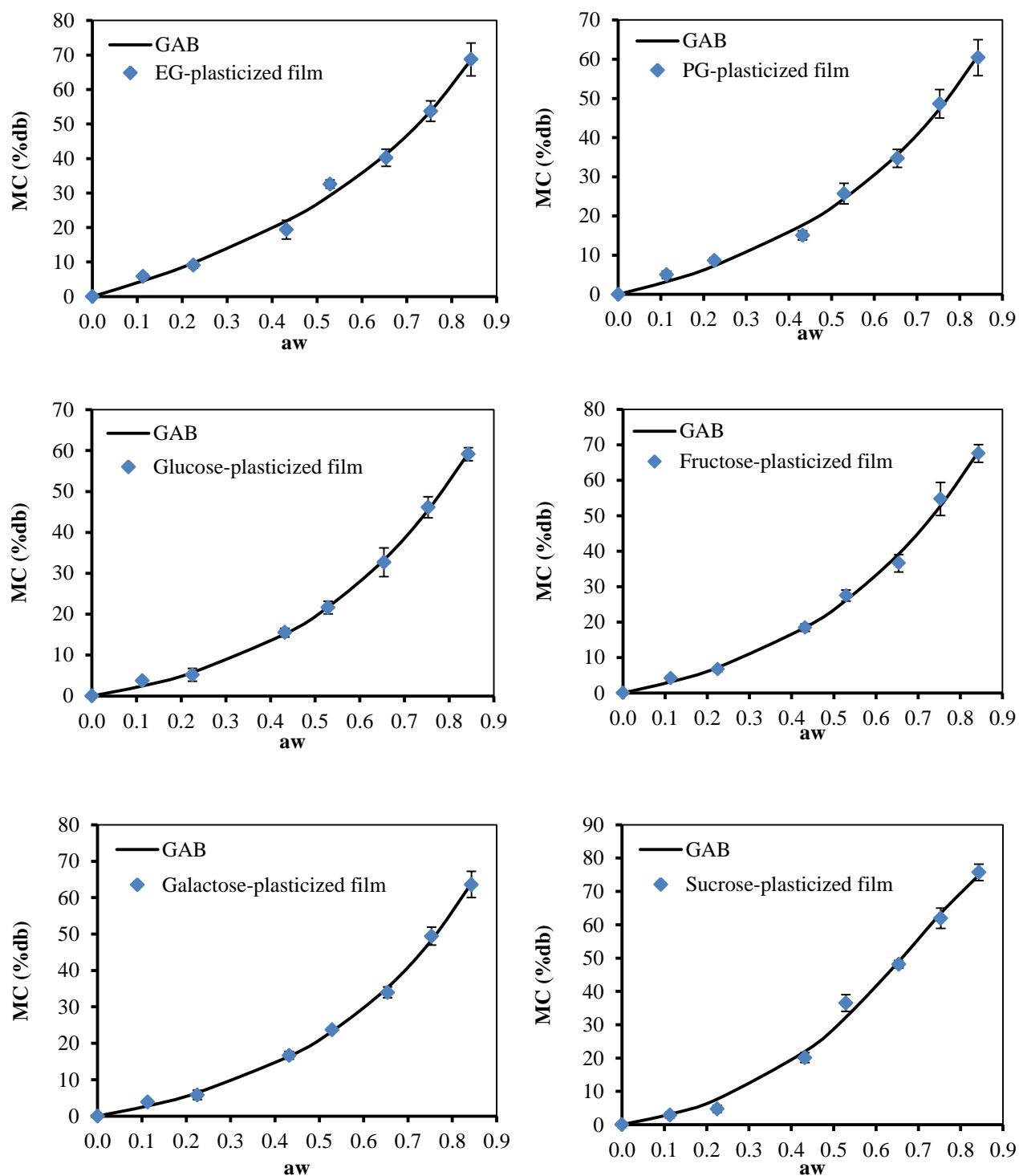


Fig. 1a. Equilibrium moisture sorption isotherm of PSGG film with different plasticizers (w/w) at 25 °C. The symbols are experimental data and the lines are from the equations obtained by fitting the experimental data to GAB equation.

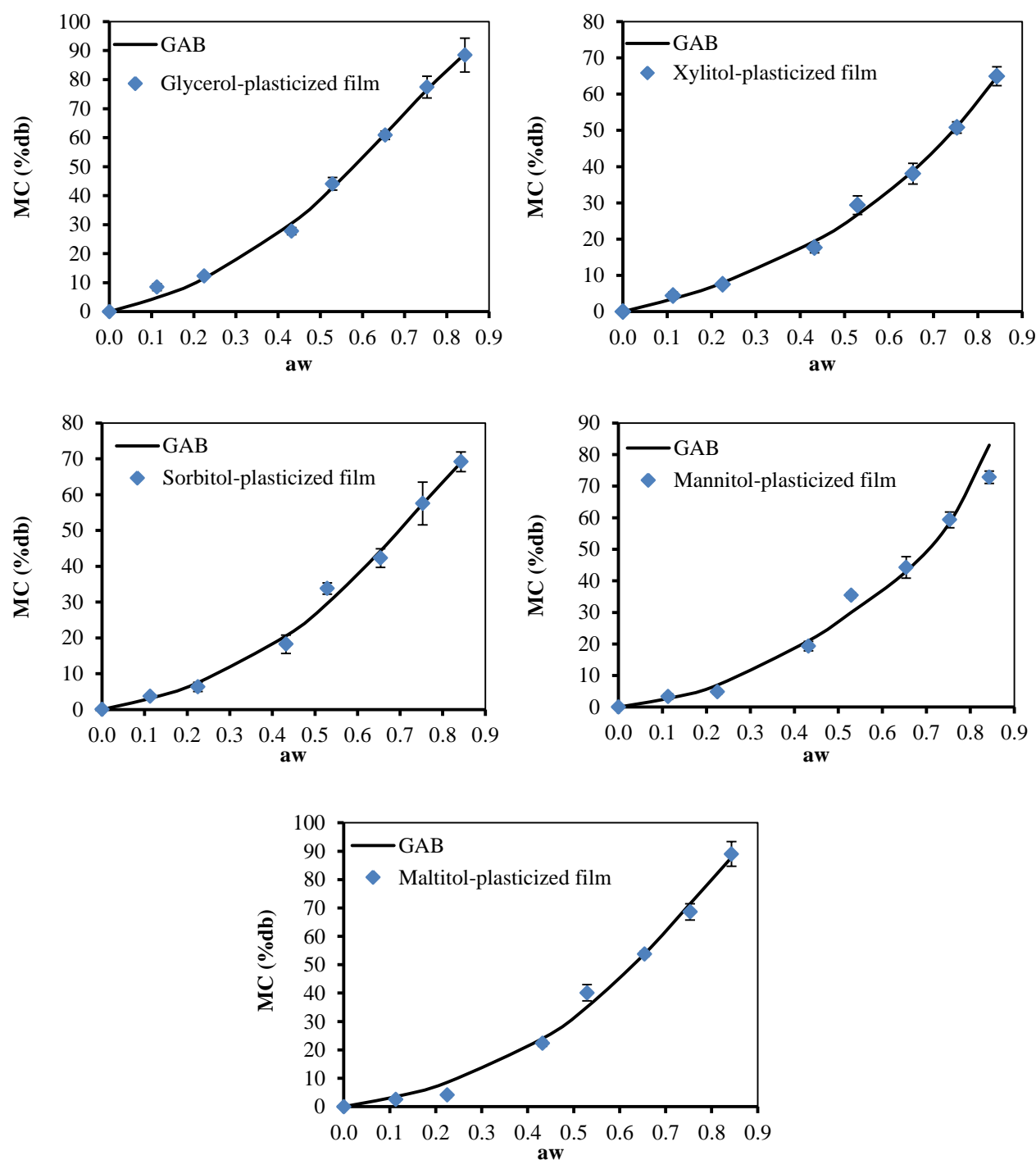


Fig. 1b. Equilibrium moisture sorption isotherm of PSGG film with different plasticizers (w/w) at 25 °C. The symbols are experimental data and the lines are from the equations obtained by fitting the experimental data to GAB equation.

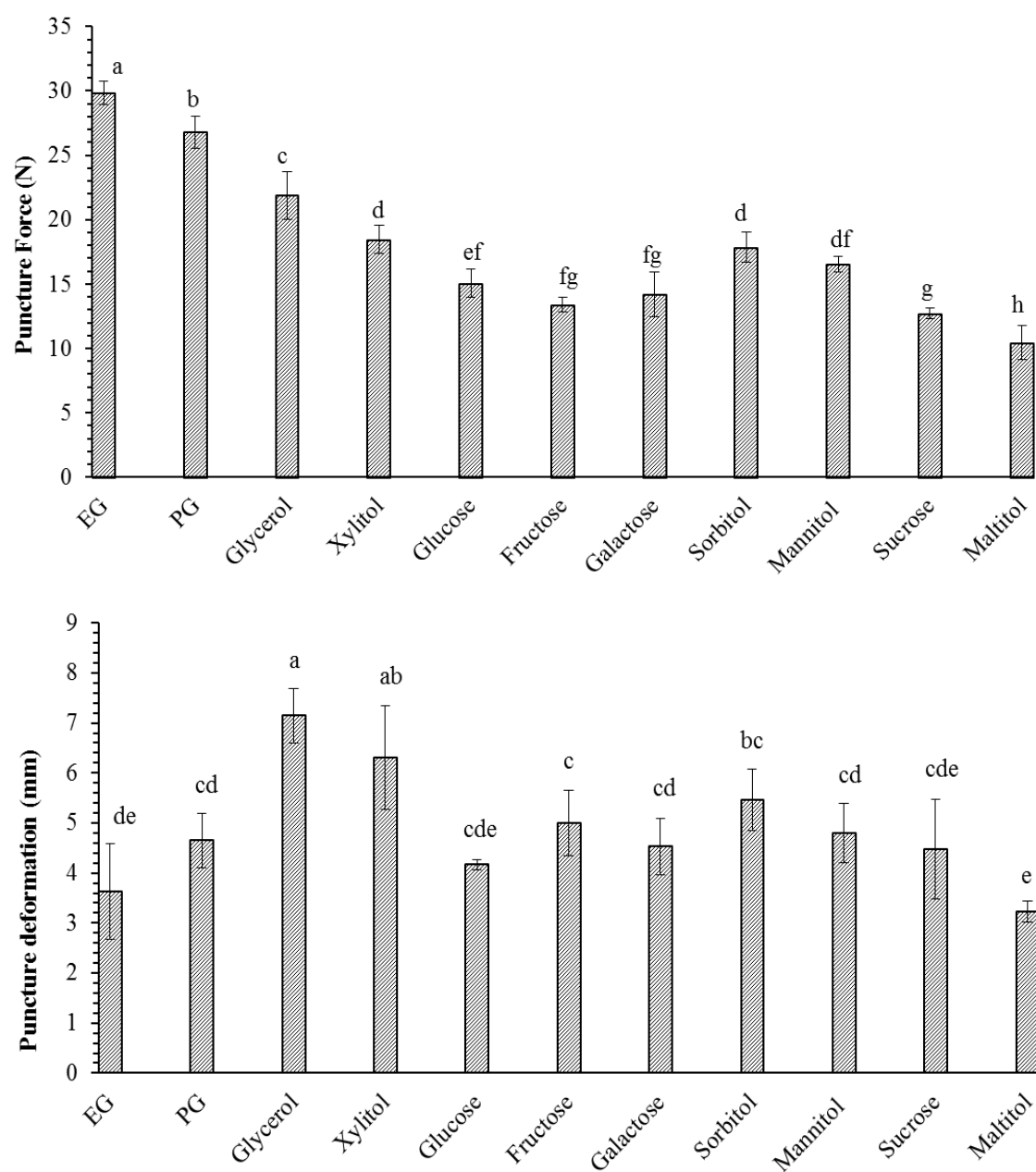


Fig. 2. Puncture mechanical properties of PSGG films with different plasticizers.

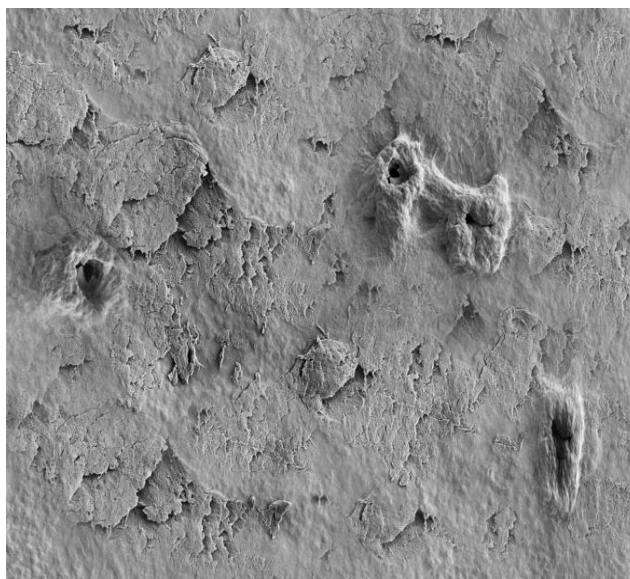


Fig. 3. Micrographs of the PSGG film without plasticizer ($\times 1000$).

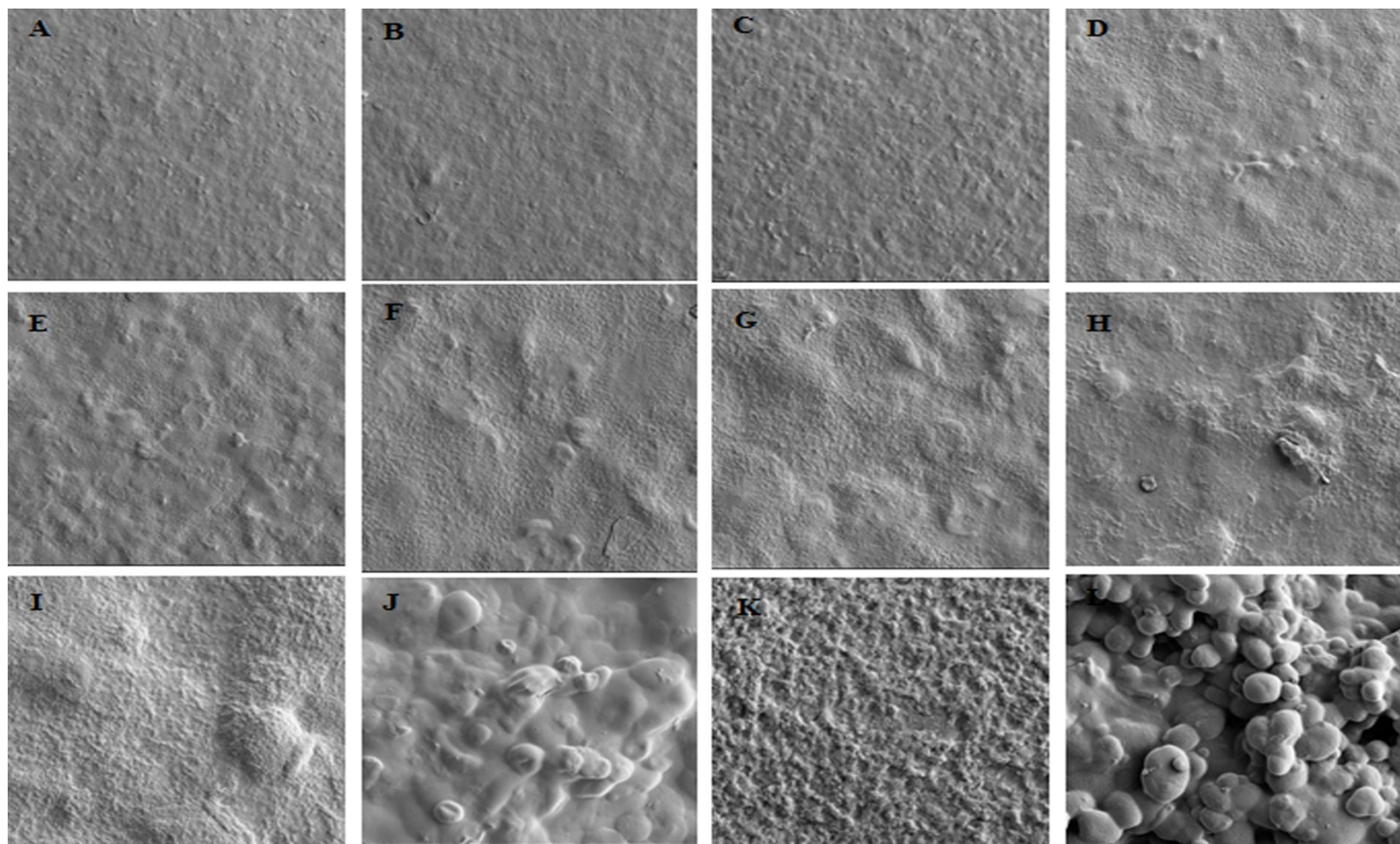


Fig. 4. Micrographs of the PSGG films ($\times 1000$). A: surface of with EG; B: surface of with PG; C: surface of with glycerol; D: surface of with xylitol; E: surface of with glucose; F: surface of with fructose; G: surface of with galactose; H: surface of with sorbitol; I: surface of with mannitol; J: surface of with sucrose; K: surface of with malitol; L: surface of with PEG-400.

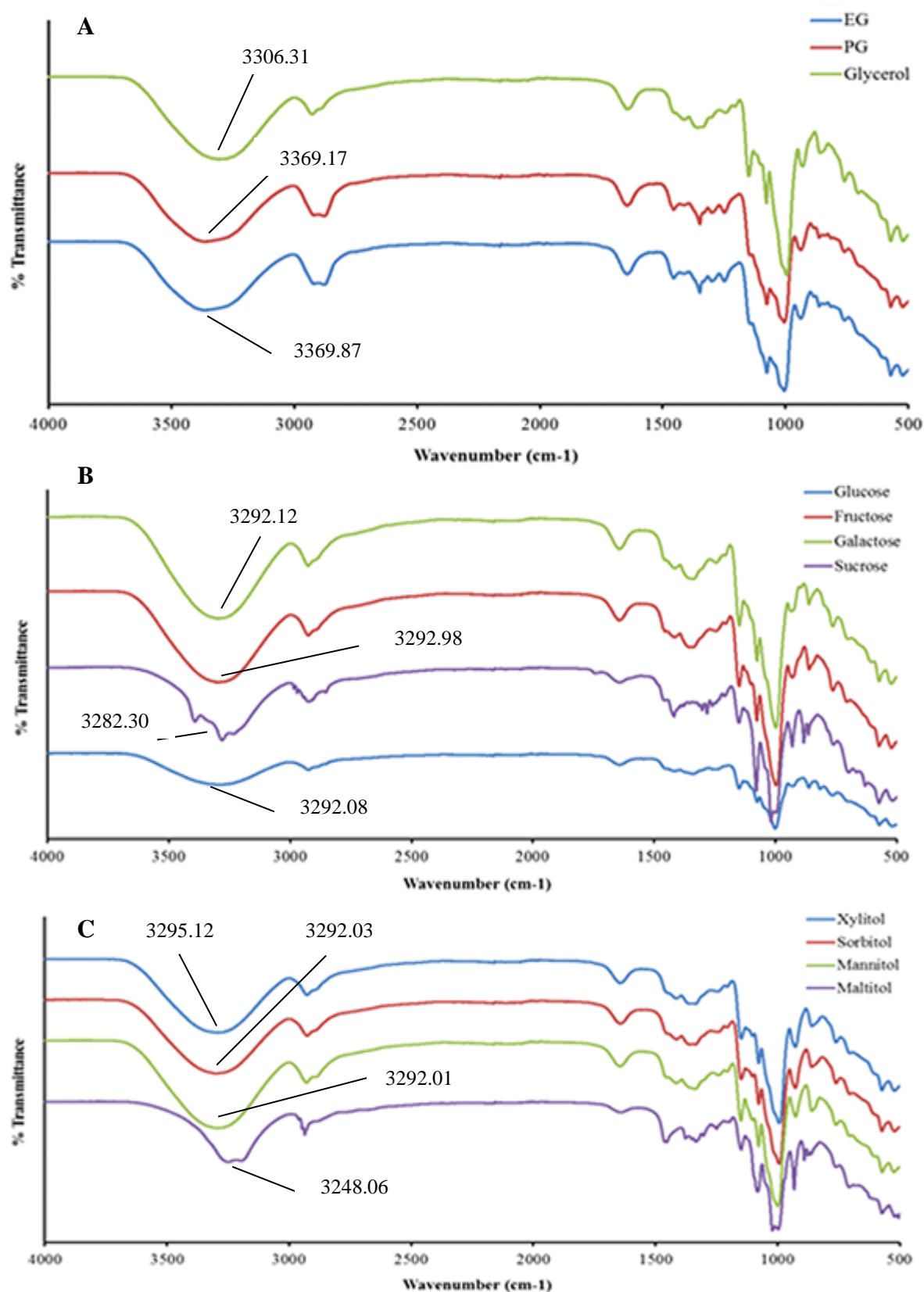


Fig. 5. FTIR spectra of PSGG films containing different plasticizers in the region 400-4000 cm^{-1} .